Modelling oxygen self-diffusion in UO2 under pressure

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Abstract: Access to values for oxygen self-diffusion over a range of temperatures and pressures in UO2 is important to nuclear fuel applications. Here, elastic and expansivity data is used in the framework of a thermodynamic model, the cBΩ model, to derive the oxygen self-diffusion coefficient in UO2 over a range of pressures (0 to 10 GPa) and temperatures (300 K to 1900 K). The significant reduction in oxygen self-diffusion as a function of increasing hydrostatic pressure, and the associated increase in activation energy, is identified.

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September 1, 2015

Dear Editor,

I wish to resubmit the manuscript *"Modelling oxygen self-diffusion in UO_2 under pressure*" to be considered for publication in *Solid State Ionics*. We wish to thank the referees for the support and the useful minor revisions, which we have now addressed. Thank you for your continued consideration of this manuscript.

Yours sincerely,

Alexander Chroneos

Reviewers' comments:

Reviewer #1: The paper represents a solid and important step forward in using a range of modelling methods to better predict nuclear materials. I recommend no major changes and just ask the authors to consider the following:

We thank the referee for the support and the useful comments.

- A reference is probably required for the statement that oxygen vacancy mechanisms are dominant in UO2.

We agree and have now added the following references:

[16] H. Matzke, J. Chem. Soc. Faraday Trans. 2 (1987) 1121.
[17] E. Vathonne, J. Wiktor, M. Freyss, G. Jomard, M. Bertolus, J. Phys.: Condens. Matter 26 (2014) 325501.

- The authors mention that this process does not work for UO2+x, could they expand on this and suggest a route forward (as all manufactured fuel is UO2+x)?

We have added the following to account for this comment:

"*In hyperstoichiometric UO_{2+x} the cBΩ model could be applicable but with a different c^{act}.*"

- I presume the same mechanism will work in UO2-x. What will happen in the mixed (U,Pu)O2-x systems?

Yes there should be equivalent mechanisms and model description for the mixed oxide systems. We are presently working on these issues.

- If I am correct, the model predicts a higher E_a under pressure. Is this kind of result mirrored using other techniques such as nudged elastic band theory? Are there any references to this?

We cannot find anything for hydrostatic pressure but only equivalent results for biaxial strain. For example, please refer to Goyal *et al.* Phys. Rev. B 91 (2015) 094103. We have added this reference in the paper.

Modelling oxygen self-diffusion in UO_2 under pressure

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Abstract

Access to values for oxygen self-diffusion over a range of temperatures and pressures in UO_2 is important to nuclear fuel applications. Here, elastic and expansivity data is used in the framework of a thermodynamic model, the cBΩ model, to derive the oxygen self-diffusion coefficient in UO_2 over a range of pressures (0 to 10 GPa) and temperatures (300 K to 1900 K). The significant reduction in oxygen self-diffusion as a function of increasing hydrostatic pressure, and the associated increase in activation energy, is identified.

Keywords: UO_2; self-diffusion; pressure

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1. Introduction

The principal component of conventional nuclear fuel is UO_2, which can be blended with other actinide oxides such as ThO_2 and PuO_2 to form mixed oxide (MOX) fuel [1,2]. Due to the inherent challenges of working with nuclear materials, atomic scale simulations have, for decades, provided comprehensive data on the properties of nuclear fuel materials, complementing experimental results [3-5].

The association of the defect Gibbs energy (g^i) and bulk properties in solids has led to a number of thermodynamic models, including the cBΩ model by Varotsos and Alexopoulos [6-8]. The latter model proposed that g^i is proportional to the isothermal bulk modulus B and the mean volume per atom [6-8]. The cBΩ model has been employed successfully to describe point defect processes in numerous materials including self-diffusion in oxides, semiconductors and metals [9-14]. In a recent study the cBΩ model was used to describe oxygen self-diffusion in UO_2 and ThO_2 over the temperature range 2000-3000 K [15].

Oxygen self-diffusion in UO_2 is facilitated by the vacancy mechanism and therefore the cBΩ model is appropriate as it is typically applied to materials with a single diffusion mechanism operating over a range of temperatures [16,17]. Here we employ the cBΩ model to derive relations for oxygen self-diffusion coefficients in UO_2 from 300 - 1900 K and 0 - 10 GPa.

2. Methodology

2.1 Molecular dynamics (MD)

Cooper *et al.* [18] have provided a comprehensive potential set (the CRG potentials) that reproduce the thermomechanical and thermophysical properties of AmO_2, CeO_2, CmO_2, NpO_2, PuO_2 [19], ThO_2 and UO_2 over a wide temperature range

(300-3000 K). The CRG potential model introduces many-body interactions using the embedded atom method (EAM) to describe the elastic constants of actinide oxides, reproducing the Cauchy violation and the bulk moduli [18,19]. Furthermore, the efficacy of this model has been demonstrated in the calculation of diffusion properties in CeO_2, $U_{1-x}Th_xO_2$ and $Pu_{1-x}U_xO_2$ [18-21]. Implementing this model, MD calculations were carried out using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [22] to investigate the variation of bulk modulus as a function of pressure. Using a UO_2 supercell of $10 \times 10 \times 10$ fluorite unit cells, calculations were carried out in the NPT ensemble with Nose-Hoover thermostat and barostat relaxation times of 0.1 ps and 0.5 ps and a timestep of 2 fs. For a given temperature the pressure was varied from 0 GPa to 10 GPa at 0.1 GPa intervals. At each interval the supercell was equilibrated for 10 ps with the volume and pressure averaged over the final 5 ps. As such, for a given temperature a P-V curve can be obtained (refer to Figure 1). A second order polynomial is then fitted to each P-V curve that describes P(V), the first derivative of which can be used in Eq. 1, to determine the bulk modulus:

$$B = -V\frac{dP}{dV} \quad (1)$$

where B is the bulk modulus, V is the volume and the first derivative of the P-V curve, $\frac{dP}{dV}$, is determined by analytically taking the derivative of the polynomial descibing P(V). The bulk modulus as a function of pressure and temperature are important parameters for determining defect diffusivity using the cBΩ model.

2.2 cBΩ model

In stoichiometric UO_2, oxygen self-diffusion is dominated by a vacancy-mediated hopping mechanism. The diffusion process can be described by the Gibbs

activation energy (g^{act}), which is the sum of the Gibbs formation (g^{f}) and the Gibbs migration (g^{m}) energies. The activation entropy s^{act} and the activation enthalpy h^{act} are given by [9,10]:

$$s^{act} = -\frac{dg^{act}}{dT}\Big|_{P} \quad (2)$$

$$h^{act} = g^{act} + Ts^{act} \quad (3)$$

The diffusion coefficient *D* is defined by:

$$D = fa_0^2 \nu e^{-\frac{g^{act}}{k_B T}} \quad (4)$$

Where f is the diffusion correlation factor, a_0 is the lattice constant, ν is the attempt frequency and k_B is Boltzmann's constant.

Using the cBΩ model the Gibbs defect energy g^{i} is related to the bulk properties of the material via the relation [6-8]:

$$g^{i} = c^{i} B\Omega \quad (5)$$

Employing Eqs. (4) and (5) we obtain:

$$D = fa_0^2 \nu e^{-\frac{c^{act} B\Omega}{k_B T}} \quad (6)$$

Using an experimentally-determined diffusivity D_1 value at T_1, c^{act} can be derived assuming that the pre-exponential factor $fa_0^2\nu$ can be determined. The pre-exponential factor involves the calculation of the diffusion correlation factor (dependent upon the diffusion mechanism and the crystal structure) and the attempt frequency. Provided that the elastic data and expansivity are known for temperature T_i, the diffusivity D_i at T_i can be calculated using Eq. 6 (single experimental measurement method [9,10]). It is important to consider that c^{act} is a constant and is assumed to be temperature and pressure independent [9,10]. The cBΩ model encapsulates anharmonic effects exhibited by the temperature decrease in B and by the thermal expansivity, and as such is advantageous when considering pressure and temperature variations that can impact

materials properties [23-25]. For example, in previous studies the cBΩ model has been shown to be successful in reproducing experimental self-diffusion values in diamond over a range of temperatures (1000–2800 K) and pressures (0–80 GPa) [26].

3. Results and discussion

In a recent study [15] the "mean value" method [27,28] was employed to describe oxygen diffusion in UO_2 via the cBΩ model. The following relation associates the oxygen diffusion coefficients to the isothermal bulk modulus and the mean volume per atom:

$$D_{cB\Omega}^{UO_2} = 1.277e^{-\frac{0.3052\,B\Omega}{k_B T}} \cdot 10^{-4} m^2 s^{-1} \quad (7)$$

In the present study both the expansivity and the isothermal bulk modulus data were derived using MD for the target range of temperatures and pressures. The mean volume per atom is calculated at every temperature and pressure by dividing the total volume of the unit cell by the number of atoms in the unit cell. Figure 2 shows the variation of bulk modulus, calculated from the PV curves shown in Figure 1, reported a) as a function of pressure for a set of temperatures and b) as a function of temperature for a set of pressures. Although each curve in Figure 2, be it B(T) or B(P), could be represented by a second order polynomial, it is useful to provide a single expression for B(T,P) that matches the full set of MD data:

$$B(T,P) = a + b \cdot T + c \cdot T^2 + d \cdot P + e \cdot P^2 + f \cdot P \cdot T \quad (8)$$

where a is the bulk modulus at (T = 0, P = 0), b and c represent temperature dependent terms, d and e are dependent on pressure and f accounts for a degree of interdependency between pressure and temperature. Using CurveExpert, which enables multivariable fitting, all parameters (a, b, c, d, e and f) were fitted simultaneously to the modelling bulk modulus data with a very strong agreement (r^2 =

0.997). The resultant parameters are reported in Table 1 and the functional form of equation 8 is plotted alongside the MD data in Figure 2, further demonstrating the strong correlation. As well as being used here to investigate diffusivity, a single equation that describes the UO_2 bulk modulus over a wide range of temperatures and pressures is useful to inform higher level models, such as those developed from finite element analysis.

Figure 3 shows the Arrhenius plot for oxygen self-diffusion coefficients in UO_2 for a range of pressures, derived by the cBΩ model using Eq. (7); Figure 4 presents the pressure dependence for oxygen self-diffusion coefficients in UO_2 for the temperature range considered. It is evident that hydrostatic pressure significantly decreases oxygen self-diffusion coefficients in UO_2. The trend in the diffusivities is similar to what was previously calculated using the cBΩ model to investigate self-diffusion in diamond under pressure [26]. Interestingly, pressure also impacts the activation energies (E_a) of oxygen diffusion (shown by the change in the slope of Fig. 3 with respect to pressure) as shown in Fig. 5. The dependence of E_a with respect to pressure is described by:

$$E_a = 5.66 + 0.123 \cdot P - 0.00356 \cdot P^2 \quad (9)$$

Considering that the activation volume is defined by $v^{act} = -\left(\frac{\partial g^{act}}{\partial P}\right)_T$, by differentiating Eq. 4 the activation volume can be calculated from:

$$v^{act}(P,T) = -k_B T \left(\frac{\partial lnD}{\partial P}\right)_T \quad (10)$$

where $\left(\frac{\partial lnD}{\partial P}\right)_T$ is the slope of Figure 4. v^{act} is then 8.75-10.66 10^{-6} m^3mol^{-1} over the temperature range 700-1500 K. This variation is significant and more pronounced than for other materials such as for example diamond (3.26-3.37 10^{-6} m^3mol^{-1} over the temperature range 1800-2600 K) [26].

Having established the validity of the cBΩ model for UO_2, other defect properties can be calculated over a wide temperature and/or pressure range. As discussed in a previous study [15], beyond the superionic transition temperature the oxygen diffusivity in UO_2 can also be modelled within the cBΩ model but with a different c^{act}. Finally, a note of caution: when considering hyperstoichiometric UO_{2+x} formation, Eq. 7 will not be valid as it refers to oxygen-vacancy-mediated migration, whereas in UO_{2+x} oxygen transport is mediated by interstitial species. In hyperstoichiometric UO_{2+x} the cBΩ model could be applicable but with a different c^{act}.

4. Conclusions

Using MD the variation of the UO_2 bulk modulus as a function of temperature and pressure, B(T,P), is examined and expressed in a single equation. Consequently, we have employed the cBΩ model to calculate oxygen self-diffusion in UO_2 over a range of pressures and temperatures. Hydrostatic pressure significantly decreases the oxygen self-diffusion coefficients in UO_2. Additionally, the activation energies for oxygen self-diffusion increase with increasing pressure. The efficacy of the cBΩ model to describe UO_2 over a wide range of pressures and temperatures encourages the investigation of other technologically important actinide oxides. While there is limited experimental data for other systems, the present study demonstrates that the cBΩ model can be used in synergy with MD derived data to make estimates of point defect properties in UO_2 over a range of pressures and temperatures.

Acknowledgements

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Table 1. Summary of the derived coefficients a, b, c, d, e and f of Eq. 8, that describe the bulk modulus of UO_2.

a (GPa)	b ($GPa \cdot K^{-1}$)	c ($GPa \cdot K^{-2}$)	d	e (GPa^{-1})	f (K^{-1})
218.0	-4.330×10^{-2}	-1.846×10^{-6}	5.864	-1.387×10^{-1}	1.301×10^{-3}

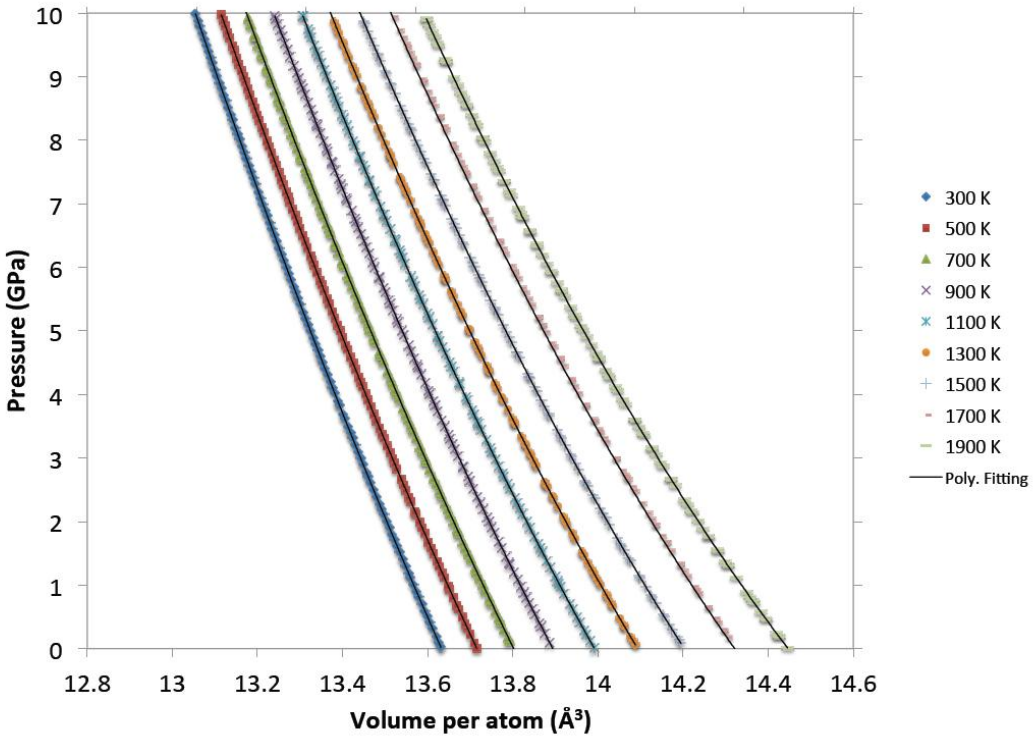
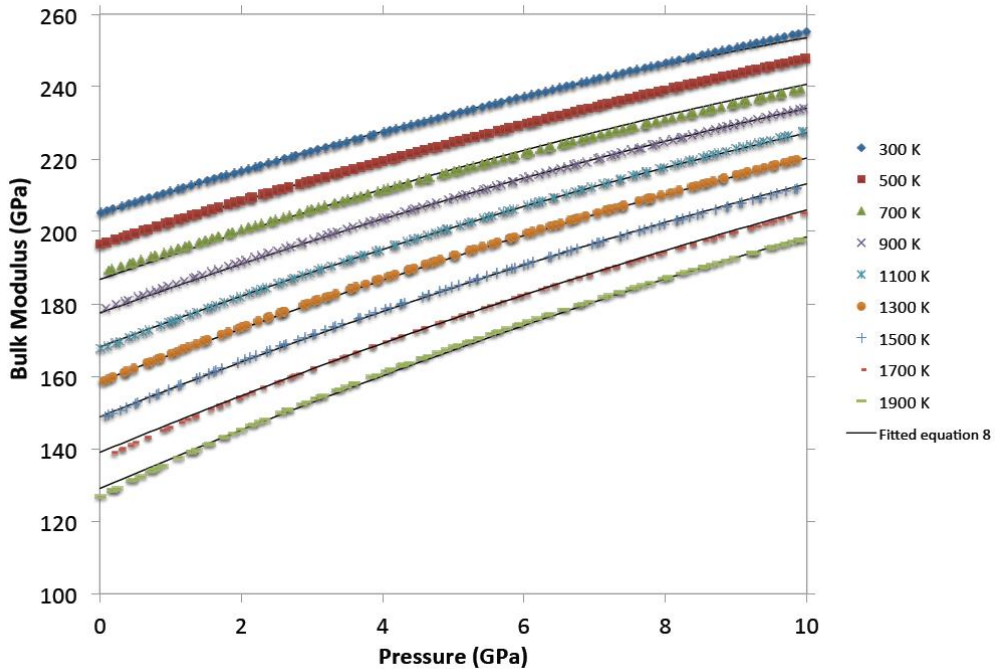


Figure 1. The variation of pressure as a function of volume per atom for UO_2 determined using MD simulation. Second order polynomials fitted to this data that were used to determine the bulk modulus as function of pressure are also shown.

a)



b)

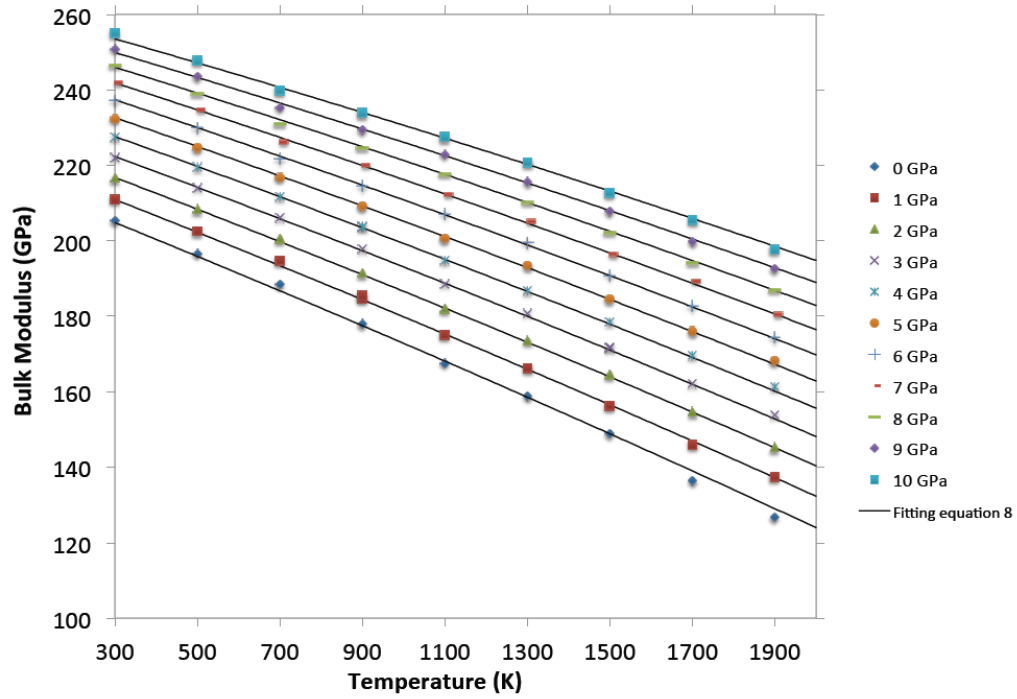


Figure 2. The bulk modulus of UO_2 from the CRG model as a function of a) pressure and b) temperature. Equation 8 is shown alongside the modeling data using the parameters reported in Table 1.

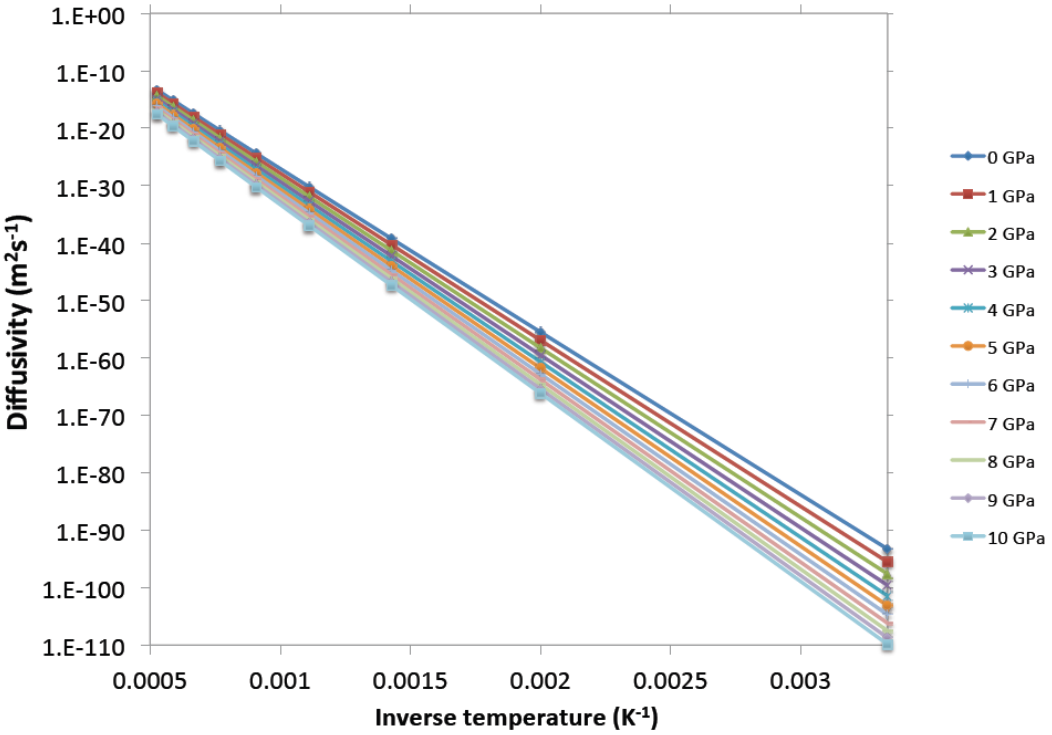


Figure 3. Arrhenius plot for oxygen self-diffusion coefficients in UO_2 derived by the cBΩ model for a range of pressures.

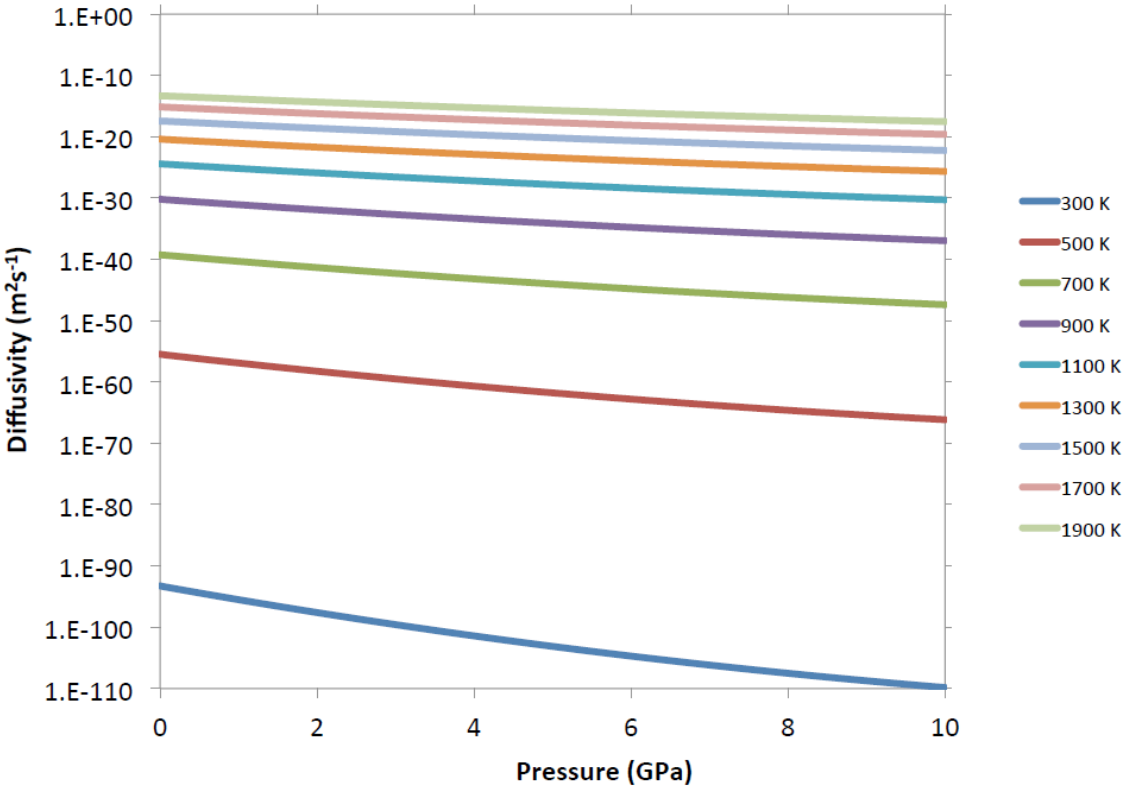


Figure 4. The pressure dependence for oxygen self-diffusion coefficients in UO_2 derived by the cBΩ model for T = 300-1900 K.

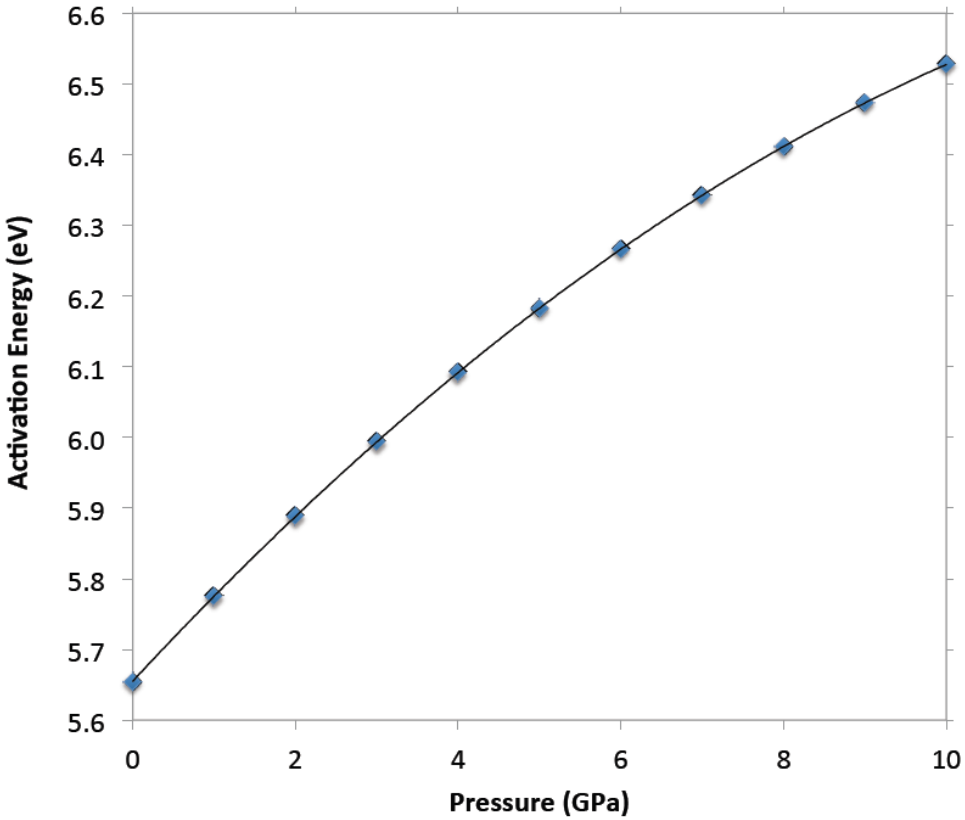


Figure 5. The pressure dependence of activation energies of oxygen diffusion in UO_2.

Highlights

1. Oxygen self-diffusion over a range of temperatures and pressures is important in UO_2.

2. The UO_2 bulk modulus as a function of T and P is expressed in a single equation.

3. The cBΩ model is used to derive the oxygen self-diffusion with respect to P in UO_2.

4. Advancing proliferation-resistant technologies to harvest the energy potential of spent fuel.